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Collective Nature of Orbital Excitations in Layered Cuprates in the Absence of Apical Oxygens

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We have investigated the 3*d* orbital excitations in $\mathrm{CaCuO_2}$ (CCO), $\mathrm{Nd_2CuO_4}$ (NCO), and $\mathrm{La_2CuO_4}$ (LCO) using high-resolution resonant inelastic x-ray scattering. In LCO they behave as well-localized excitations, similarly to several other cuprates. On the contrary, in CCO and NCO the d_{xy} orbital clearly disperses, pointing to a collective character of this excitation (orbiton) in compounds without apical oxygen. We ascribe the origin of the dispersion as stemming from a substantial next-nearest-neighbor (NNN) orbital superexchange. Such an exchange leads to the liberation of the orbiton from its coupling to magnons, which is associated with the orbiton hopping between nearest neighbor copper sites. Finally, we show that the exceptionally large NNN orbital superexchange can be traced back to the absence of apical oxygens suppressing the charge transfer energy.

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Introduction.—Strongly correlated electron materials display simultaneously the presence of a strong, localizing repulsion between the *d* electrons of the metal cations and large hopping integrals mediated by the ligand anions, which instead tend to delocalize the carriers [1]. These opposite tendencies lead to the appearance of a plethora of electronic orders and broken symmetries, as well as the emergence of collective excitations with various quantum numbers and complex origin [2–4].

Understanding the possible onset of such collective excitations is particularly challenging in the case of the *d*-orbital excitations. On one hand, the large hopping elements give rise to dispersive bands enumerated by the *d*-orbital quantum numbers. On the other hand, the strong Coulomb repulsion suppresses charge mobility and favors local, atomiclike, orbital excitations. In fact, it has been widely believed that the orbital (*dd*) excitations in the Mott insulating two-dimensional (2D) cuprates are purely local and well-described using the single-ion picture [5]. Here we show that, similarly to electronic charge [6,7] and spin [8–10], also the cuprate *d*-orbital degree of freedom *can* display a collective nature—for we observe the long-sought collective orbital excitations (orbitons) [11,12] in $\mathrm{CaCuO_2}$ (CCO) and $\mathrm{Nd_2CuO_4}$ (NCO).

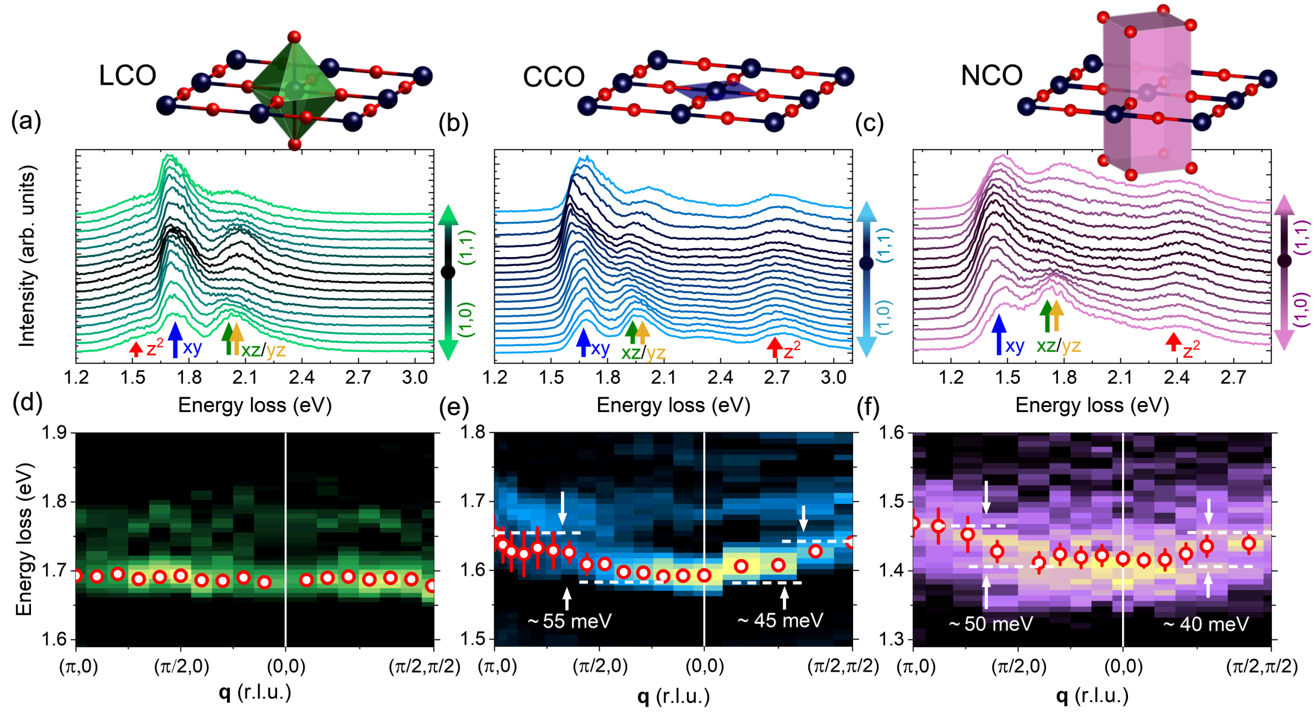

FIG. 1. Overview of the Cu L_3 RIXS data, measured with σ incident polarization, for LCO, CCO and NCO. Panels (a)–(c): below the respective scheme of the Cu coordination, we show the stack of RIXS spectra as a function of momentum $\mathbf{q}$ along the (1,0) and (1,1) directions. The labels indicate the symmetry of the peaks as determined from comparison with single-ion calculations [5,35]. (d)–(f): map of the second derivative of the scans of panels (a)–(c), an enlarged view of the energy range of the *xy* excitation. Red dots highlight the position of local maxima, which correspond to a peak in the original RIXS scans. Note that the energy scale is the same in the three panels although centered at different absolute energies.

Evidence of collective orbital excitations (orbitons) has been found in one-dimensional (1D) cuprates, where the reduced dimensionality leads to the fractionalization of the electron, i.e., the effective separation of its charge, spin, and orbital components that can propagate independently from each other. Experiments on chain and ladder cuprates [13–15]) as well as calculations [16–18] have shown that the exciton formed by the promotion of an electron to a higher-energy *d* orbital can propagate coherently through the antiferromagnetic (AFM) background, in a very similar fashion to a single hole in the AFM state [19,20]. The resulting excitation leads to a lenslike dispersion map, with a dominant signal at its lower edge displaying a maximum in energy at the Γ point and a minimum at the magnetic zone boundary [13,15].

In two-dimensional (2D) and three-dimensional (3D) compounds, the fractionalization of electrons is still under debate. In AFM systems, the motion of the orbiton generates a "trail" of magnetic excitations that prevents the independent propagation of spinons and orbitons [21,22]. In Kugel-Khomskii systems with ferromagnetic (FM) order, and therefore no coupling between orbitons and magnons, a theoretical prediction that *disregards* coupling to the lattice suggests the possibility of itinerant orbitons [23]. However, the coupling to the lattice, which is stronger in 2D and 3D, further hinders the orbiton motion [24–26]. In fact, the extensive experimental search for orbitons in the FM manganites and titanates [25,27–29] has so far been inconclusive. In layered cuprates, the parent compounds of high-T_c superconductors with 2D AFM order, orbital excitations have always been found to be localized in nature and interpreted as atomic transitions in the presence of a ligand field [5,30]. More in general, apart from the "special" 1D case mentioned above, dispersing orbitons in 3*d* transition-metal oxides have remained elusive [31], resulting in a striking asymmetry between magnetic and orbital excitations [33]. In this Letter, we report Cu L_3-edge resonant inelastic x-ray scattering (RIXS) measurements of the orbital excitations in three cuprate families: the single-layer La_2CuO_4 (LCO) and Nd_2CuO_4 (NCO), and the infinite-layer $CaCuO_2$ (CCO). While the orbital excitations in La_2CuO_4 show no sign of dispersion, in agreement with previous data [5], in CCO and NCO we observe a clear collective nature of the *dd* excitations with a dispersion larger than 50 meV along the (1,0) and the (1,1) crystallographic directions.

Experimental results.—The experiment has been performed on high-quality films of La_2CuO_4, $CaCuO_2$, and Nd_2CuO_4. Details of the preparation are described in [35–40]. Spectra of LCO and CCO were measured at the beamline ID32 [41] of the European Synchrotron ESRF, France, and those of NCO at the beamline I21 of the Diamond Light Source, UK [42]. The scattering angle was kept fixed at 150°, and in-plane momentum scans were performed by changing the incident angle θ. The energy was fixed at the copper L_3 resonance (∼931 eV). We employed incident linear-vertical (σ) and linear-horizontal (π) polarizations. The total experimental line width was ∼40 meV for CCO and LCO, ∼50 meV for NCO. The temperature was kept fixed at 20 K. The three compounds share the same in-plane CuO_2 square lattice structure but differ in the out-of-plane Cu-O coordination, as shown in the insets of Fig. 1. In LCO, the Cu^{2+} ion is directly bound to two out-of-plane (apical) oxygen atoms to form elongated octahedra. The infinite-layer CCO has no out-of-plane oxygen at all. And in the T' structure of NCO the CuO_2 planes are separated by Nd-O layers with oxygen not in the apical position but above and below the in-plane oxygens. Panels (a)–(c) of Fig. 1 display the momentum dependence of the orbital excitations in LCO (left), CCO (center), and NCO (right) along the high-symmetry directions (1,0) and (1,1), acquired with σ incident polarization. The orbital spectra are composed by three main features, which correspond to the transitions between the $(x^2\text{-}y^2)$ ground state and the other $3d$ orbitals $(xy, xz/yz, z^2)$ split by the tetragonal crystal field. The excitation energy is similar among the three compounds for the (xy) case, and differs more for the other orbitals, more influenced by the out-of-plane coordination [5]. As the first ligand-field excited state is at very high energy (∼1.5 eV), all three compounds are characterized by a rigid ferro-orbital order with $(x^2\text{-}y^2)$ symmetry. In turn, the virtual hopping of the single hole of the Cu atom determines strong AFM interactions between neighboring sites (in agreement with the Goodenough-Kanamori rules), and indeed all samples display dispersing magnetic excitations at energies $<$ 0.4 eV (not shown in Fig. 1). Their intensity evolution with momentum is mostly due to the RIXS matrix elements, which depend on photon polarization and scattering angles [5].

A closer inspection reveals that, while the energy of the peaks in LCO is independent of $\mathbf{q}$, the energy of the (xy) and xz/yx excitations shows an appreciable dispersion for CCO and NCO. For a quantitative estimation we extracted the second derivative of the RIXS spectra [Figs. 1(d)–1(f)]. For LCO the xy excitation shows no dispersion within error bars, while for CCO it exhibits a dispersion of 55 ± 15 meV and 50 ± 5 meV along the (1,0) and (1,1) directions, respectively. The energy is maximum at $(\pi, 0)$ and $[(\pi/2), (\pi/2)]$ and minimum at the Γ point (0,0). A similar, though smaller, dispersion is observed for NCO (50 ± 20 meV and 40 ± 10 meV, respectively). This behavior is at odds to what has been observed [13,15] and calculated [16] in 1D compounds, where the dd excitations' lowest energy edge disperses with a π periodicity and reaches its maximum energy at Γ. For the three samples, a satellite of the main dispersing (xy) peak, about 50–70 meV higher in energy, shows very limited or zero dispersion and an asymmetric line shape. The (xz/yz) orbital also shows a marked dispersion especially along the (1,1) direction, with again a minimum at the Γ point [see panels (b) and (c)]. Interestingly, for both CCO and NCO an additional broad feature is evident at ∼300–400 meV above the (xz/yz) peak. The momentum dependence of their integrated spectral weight is similar to that of the main (xz/yx) peak, and both agree with the single-ion calculations for that final state (see Supplemental Material [35]). These observations indicate that the (xz/yz) excitations are very broad in energy and cannot be identified with just a single, though dispersing, peak. The (z^2) excitation is quite broad too and it is more difficult to identify an associated dispersion. In previous investigations of CCO by RIXS [5,43] the dispersion of orbital excitations was overlooked either because of insufficient energy resolution (240 meV in Ref. [5]) or because the focus of the articles was on spin excitations in the mid-IR energy range, not the dd excitation in the eV range [43,44]. Here [35] we have exploited a better combination of scattering geometries (grazing incidence and reflection) and incident polarizations (σ and π) to assess the dispersion of dd excitations, and excluded that the observed effect is the result of multiple peaks at adjacent energies following different intensity dependencies on momentum.

Orbital superexchange model.—The dispersion of the dd excitation energy as a function of wavevector is so far unreported in layered cuprates, and in general in two-dimensional $3d$ transition metal compounds. Phenomenologically, the different behavior of LCO, CCO and NCO clearly correlates to the presence or absence of apical oxygens. On the theoretical level, our observations can be linked to the reduced value of Δ, the charge-transfer energy between Cu ($3d$, $4s$) and in-plane O ($2p$) states, in the absence of apical ligands [45–47]. A smaller Δ, in turn, increases the nearest-neighbor and longer-range Cu-Cu hopping amplitudes t, t' [43,46,47]. In fact, as discussed below, a similar situation concerns also the orbiton hopping elements—which turn out to be significantly increased in CCO and NCO with respect to LCO. A simple two-site model can reproduce the measured dispersion, but fails to give a proper physical description as it intrinsically neglects the presence of the underlying 2D AFM lattice (see [35]).

Our starting point is, therefore, the Kugel-Khomskii–type spin-orbital model [48], where orbital excitations can move from site to site thanks to a perturbative, three-step superexchange (SE) process [1]. In 2D and 3D AFM systems, the nearest-neighbor (NN) SE is impeded by the strong interaction between orbitons and magnons [21], what is known as magnetic string effect (see [35] for an intuitive explanation). The orbiton dispersion through this mechanism is effectively forbidden. Therefore, and further stimulated by the experimental evidence, we propose an

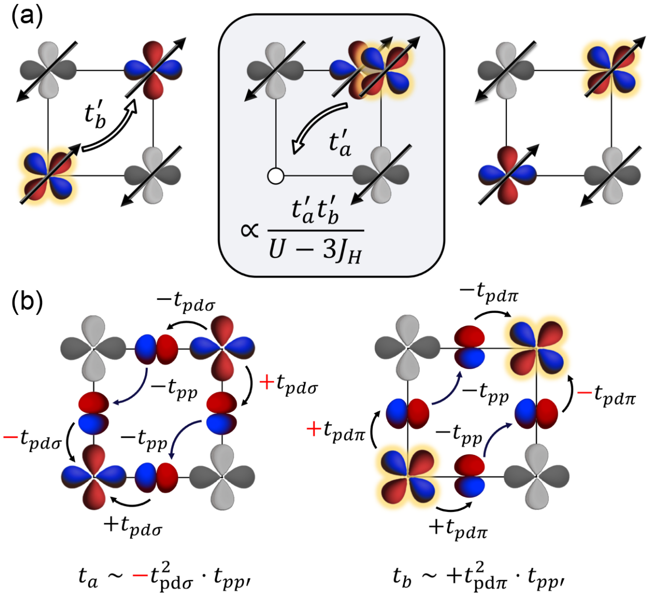

FIG. 2. (a) Schematic representation of the next-nearest neighbor (NNN) xy orbiton propagation in the hole language in 2D cuprates. The sketch on the left corresponds to the final state of the RIXS process. The total amplitude of the orbiton superexchange process is divided by the energy $U - 3J_H$ of the spin-triplet intermediate state. (b) Cartoon of the effective hopping between NNN x^2-y^2 orbitals (t_a, left panel) and xy orbitals (t_b, right panel). The "Slater-Koster" hopping terms [49] between copper and oxygen orbitals ($t_{pd\sigma}$, $t_{pd\pi}$, and t_{pp}) are defined in the usual way, cf. [17,35,50]. In both cases, the two different paths across the plaquette constructively interfere, but the number of negative signs (highlighted in red) is different in the two cases, so that $t_a t_b < 0$.

orbital SE process between next-nearest-neighbor (NNN) sites, see Fig. 2(a). We focus our analysis on the xy excitation. The xy hole can move to a NNN site through a hopping integral t'_b; the NNN site becomes thus occupied by two holes with different symmetry (x^2-y^2 and xy) and parallel spin, which costs energy $U - 3J_H$ [17]; finally the x^2-y^2 hole can move by hopping t'_a to the original site, resulting in the SE parameter $J^{\mathrm{orb}}_{\mathrm{NNN}} \propto t'_a t'_b/(U - 3J_H)$. Altogether, such an orbital SE model leads to an orbiton dispersion relation unaffected by magnons:

$$\varepsilon_{\mathbf{k}} = 2J^{\mathrm{orb}}_{\mathrm{NNN}} \cos k_x \cos k_y. \tag{1}$$

Interestingly, the sign of the $J^{\mathrm{orb}}_{\mathrm{NNN}}$ orbital exchange is always *negative* in the 2D cuprates, though its modulus depends on the crystalline structure (see below). Indeed, the sign is determined by the relative phase factors of the considered oxygen and copper orbitals, as schematized in Fig. 2(b). The Cu-Cu hopping integrals t'_a and t'_b have opposite sign, due to the distinct signs before the $t_{pd\sigma}$ and $t_{pd\pi}$ hoppings for the respective bonding copper and oxygen orbitals. Ultimately, the sign depends on the fact that the xy orbital has its lobes, and therefore phases, rotated by 45° with respect to the (x^2-y^2) orbital. It is important to note that the opposite sign of t'_a and t'_b is obtained in the cuprate charge-transfer (Emery) model, whereas in a canonical multiorbital Hubbard model this sign is assumed to be the same [1].

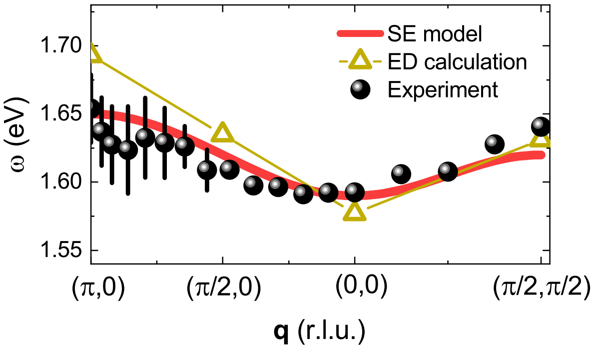

FIG. 3. Dispersion relation ε_k, for the (xy) orbiton in CCO, obtained from the RIXS experiment (points), the SE model (red line) Eq. (1), and from the numerical exact diagonalization (ED) of the multiorbital Hubbard model on a 4×4 cluster (yellow points and line). See text for further details.

Validity of the model.—As shown in Fig. 3(a), the calculated dispersion of the (xy) orbiton using Eq. (1) agrees very well with the experimental RIXS data of CCO. Note that for CCO, the relatively large oxygen-oxygen hopping $t_{pp} \approx 0.7$ eV [47,51] and small charge transfer energy $\Delta \approx 1.8$ eV [46,52–54] lead to the estimation $J^{\mathrm{orb}}_{\mathrm{NNN}} \approx -15$ meV by state-of-the-art cell perturbation theory [50] applied to the charge transfer model (see SM [35] for details, which includes Refs. [17,46,47,51,55–57]). Moreover, our model can account for the difference between LCO and the other two compounds. In fact, the presence of apical oxygens in LCO raises the charge-transfer energy to $\Delta \approx 2.6$ eV [46,58], decreases the covalency and leads to $|J^{\mathrm{orb}}_{\mathrm{NNN}}| < 6$ meV, i.e., at least two-and-a-half times smaller than in CCO [35]. The presence of apicals should also decrease the oxygen-oxygen t_{pp} [35], further reducing $|J^{\mathrm{orb}}_{\mathrm{NNN}}|$. This explains why the orbiton dispersion in LCO falls below the current experimental sensitivity.

To verify the assumption that orbiton and magnons effectively decouple [which has lead to Eq. (1)], we performed exact diagonalization (ED) of a realistic multiorbital Hubbard model [35]. Such calculations inherently account for all possible SE processes, including magnon-orbiton coupling. The latter could lead to spectral weight transfer from the orbiton quasiparticle to the continuum and to a renormalization of the orbiton dispersion [16,21,22,34]. Both effects, as shown in the Supplemental Material [35], turn out to be very small. The dispersion calculated with the ED calculations follows semiquantitatively the one predicted with the SE model, and is reported with yellow triangles in Fig. 3. Moreover, the surprisingly small incoherent part of the ED spectrum is barely visible in the asymmetric shape of the line spectra, as reported in the Supplemental Material [35]. This good agreement is due to the different kinetic energies of the magnon and the orbiton (the former being faster than the latter) and to the dominant NNN orbital exchange.

As explained above, the experimental spectra also reveal the presence of a nondispersing peak ~70 meV above the dispersing *xy* excitation. The ED calculation shows indeed the presence of a continuum of magnetic origin caused by the NN SE interaction, but underestimates its intensity as described in the Supplemental Material [35]. Another probable explanation is in terms of a ladder spectrum consisting of orbitons coupled to phonon satellites, which are always present in the *dd* excitation spectra [59]. The energy separation between the dispersing and the nondispersing *xy* peak indeed agrees with the energy of bond-stretching oxygen modes [60], which possess the strongest electron-phonon coupling among all branches and indeed dominate the low-energy RIXS response (see Supplemental Material [35]). The dispersionless nature of the satellite peak can be rationalized by noting that, not only coupling the mobile orbitons to a massive local excitation would strongly reduce its dispersion [61–64], but even in case of coupling to dispersive (e.g., acoustic) phonons the observed dispersion is strongly renormalized and below our sensitivity—as realistic calculations for coupling of cuprate electrons to phonons reveal [65,66]. Moreover, the unavoidable presence of multiple phonon harmonics (ladder spectrum) explains the asymmetric line shape of the nondispersing peak.

Conclusions.—The observation of a sizable dispersion of orbital excitations in cuprates without apical oxygens demonstrates that *dd* excitations can have a collective nature beyond the 1D case. The large orbiton dispersion is a consequence of a significant NNN orbital SE. Unlike the NN one, the NNN exchange takes place on the same AFM sublattice and allows for an almost free orbiton hopping, i.e., without coupling between orbitons and magnons. This mechanism is different from the 1D case, where the orbiton hops between NN copper sites and decouples from the magnetic excitations solely due to the fractionalization of electrons in the 1D interacting systems [13,16]. Such fractionalization in the orbital sector is instead absent in our 2D case. The narrower orbiton bandwidth in 2D with respect to the 1D cases might be due to a smaller superexchange interaction [13,44,67] following a larger charge-transfer energy [68], but further studies are required for an exhaustive understanding of the phenomenon.

The exceptionally large NNN orbital superexchange can be traced back to the strong copper-oxygen covalency in the copper oxides without apical oxygens [46]. We note that longer-range hopping is at the origin of the peculiar properties of spin excitations of CCO, with spinonlike behavior emerging close to $(\pi, 0)$, in analogy to 1D spin systems [44]. It turns out that a canonical Hubbard-like description cannot yield the observed sign of the orbital superexchange. One has to go "back" to the charge transfer (Emery) model to get this sign correct, highlighting the fundamental role played by oxygen bands in the physics of 2D cuprates. Lastly, the observed mobility of orbitons might explain the measured coupling between *dd* excitations and doped holes [30,69]. Recently, it has been demonstrated that such coupling can lead to an attractive interaction between holes, positively contributing to superconducting pairing [70]. It would therefore be of interest to explore the effect of doping on the dispersion of orbital excitations.

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